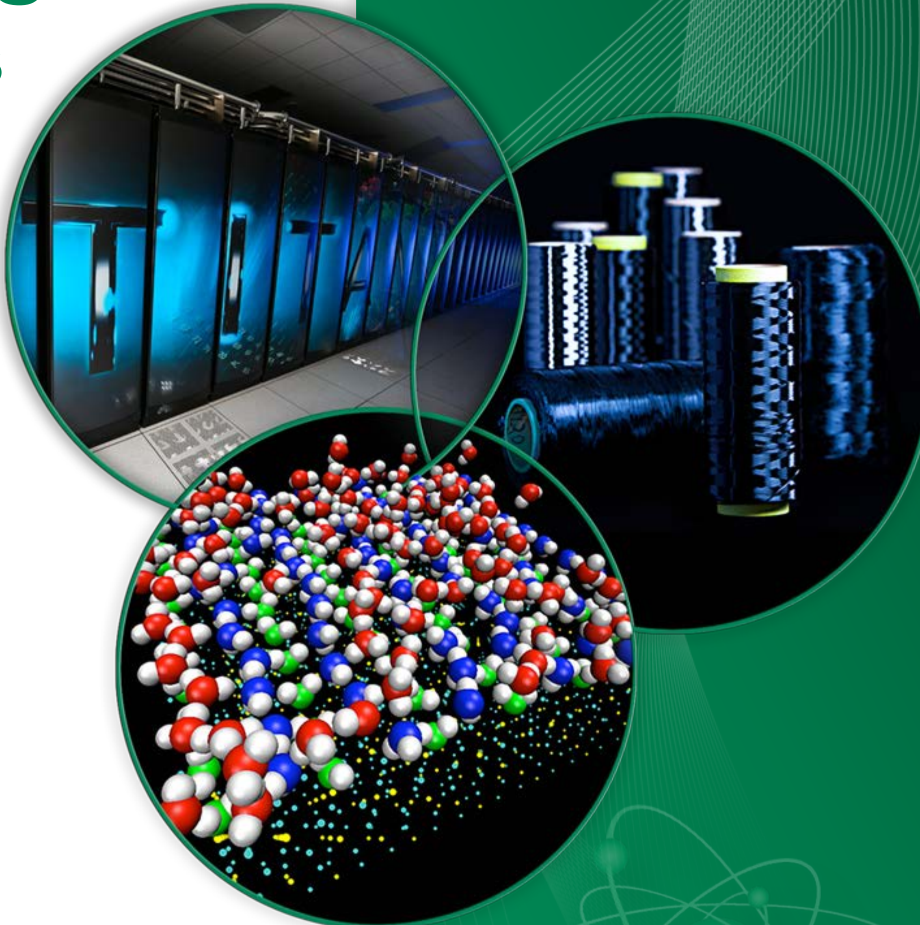
Studies on Lithium Manganese Rich MNC Composite Cathodes



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Oak Ridge National Laboratory

16th May 2013

Project ID # ES106

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Overview

Timeline

- Project start date : Oct. 2010
- Status : Continuing

Barriers

Performance: High energy density for EV and 40 mile PHEV & beyond.

Life : More that 5000 deep discharge (SOC range) over the entire life.

Abuse Tolerance: Thermally stable high energy Li-ion couples.

Budget

- FY 2011 400K
- FY 2012 400K
- FY 2013 400K

Partners

National Labs

S. K. Martha & Nancy Dudney; ORNL

Chris Johnson, Daniel Abraham & Tony Burrell

Argonne National Lab

Joy Andrews

Stanford Synchrotron Radiation Lab, SLAC, CA.

Industrial:

Andy Drews & Dawn Bernardi

Ford Motor Company

Mr. Toyoji Sugisawa

Toda America Inc.

Project Objectives - Relevance

Undertake advanced materials research in the area of high energy (capacity) electrode materials for lithium-ion couples with following objectives

- Enable/accomplish DOE-Energy Storage technical target in terms of cell level energy densities (volumetric & gravimetric); EV and 40 mile PHEV & beyond
- Identify the capacity & cycle-life fade mechanisms in relevant high capacity lithium-ion chemistries and develop methods for mitigation.
- Apply & develop materials & electrochemical characterization methods at a cell or electrode level: "Local state-of-charge studies"

Milestones

FY2012

Due Date	Description	Status
Oct 2011- March 2012	Electrochemical performance benchmarking and rate performance improvement of LMR-NMC (vs Li)	Complete
May 2012	EIS studies & materials characterization of LMR-NMC materials and electrode	Complete
Sep 2012	Improving the interfacial stability of LMR-NMC by Lipon coating and performance testing .	Complete

FY2013

Due Date	Description	Status
Oct 2012- Jan 2013	Perform full cell studies of LMR-NMC with A-12 graphite for studying capacity & voltage fade	Currently in progress
March 2013	Electron microscopy & local SOC studies of LMR-NMC	In progress
Sept. 30, 2013	Quantifying voltage fade in LMR-NMC full cells and develop mitigation routes	On Schedule

Approach/Strategy-I

I. Undertake a comprehensive materials based approach to address issues in lithium manganese rich NMC (LMR-NMC) high voltage cathodes.

Observed cell level performance limitation or failure	Origin (Materials based)	Mitigation Strategy	Status
High ASI at low SOC	Poor electronic & ionic conductivity	Carbon coating or nanofiber addition, composition variation	Completed
Capacity fade under continuous high V cycling (> 4.5V) @ 25 and 60 °C	Interfacial stability, electrolyte oxidation, surface film formation, TM dissolution	Surface coating, limiting SOC window, electrolyte additives	70 % complete
Voltage fade under continuous high V cycling (> 4.5 V)	Structural instability, phase changes	New synthesis approach, composition tuning and isovalent substitution	In progress

Approach/Strategy-II

II. Benchmark /standardize results as per ABR or BATT protocol (methods)

Progress FY-12 &13: Collaboration with ABR team on voltage fade of LMR-NMC

(i) Initiated common testing protocols on standard electrodes and cathode materials.

(ii) Data and information exchange

III. Develop a fundamental (atomic) level understanding of the structural changes induced during 1st cycle and subsequent high voltage cycling if LMR-NMC and other high energy density cathode composition .

Progress FY-12 &13: (i) High resolution electron microscopy & EELS study of pristine & cycled LMR-NMC cathodes.

(ii) TXM-XANES study to map the Mn, Ni & Co oxidation states as a function of cycling. (with SSRL Stanford)

Approach for Coating on LMR-NMC

Goal-I : Improve the cycle life and interfacial stability of LMR-NMC cathode by coating a nanometer thick solid electrolyte; Lithium Phosphorus Oxynitride (Lipon).

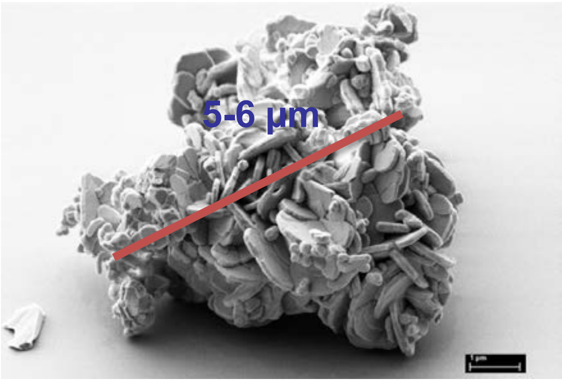
Goal-II : Whether coating LMR-NMC at a particle or electrode level can eliminate or slow down the voltage fade in LMR-NMC.

Goal-III : Why coatings on electrodes provide improved performance ?: Microstructural & electrochemical performance analysis

Background

Comparing LMR-NMC Particle Morphology & Composition

ABR Program

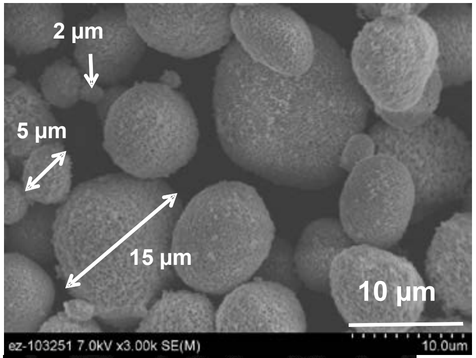


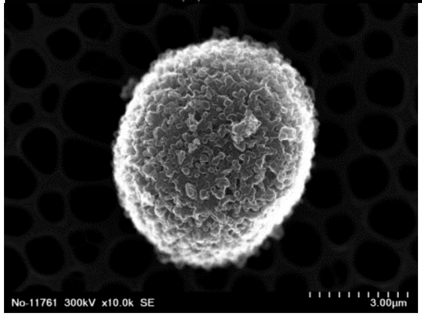
$Li_{1.2}Mn_{0.55}Ni_{0.15}Co_{0.1}O_2$ (HE5050)

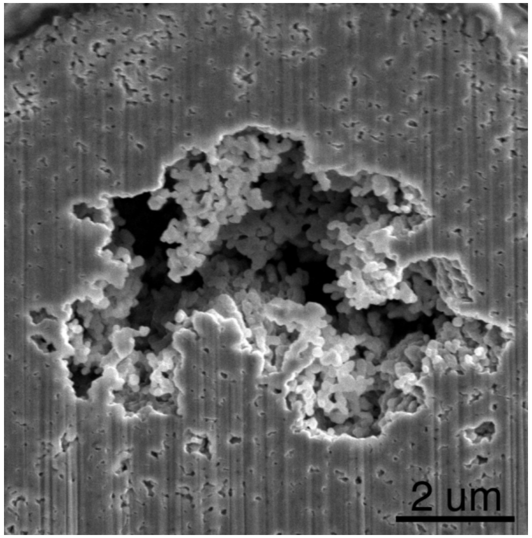
($0.5Li_2MnO_3$ - $0.5LiNi_{0.375}Co_{0.25}Mn_{0.375}O_2$
in the 2-component notation)

Courtesy : Daniel Abraham, ANL

This study







$Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}O_2$ or $0.6Li(Li_{1/3}Mn_{2/3})O_3$-$0.4Li[Mn_{0.3}Ni_{0.45}Co_{0.25}])O_2$

Electrochemical performance could depend upto some extent on the starting precursor & synthetic route due to change in

- Particle size & morphology at the primary and aggregate level.
- Tap density.
- Nominal change in composition.

Technical Accomplishment

Coating Lipon on LMR-NMC Cathode Material

Advantage of using Lipon

- Electrochemical stability window up to 5.5 volts and hence good for 5 V chemistry.
- Reasonable room temperature Li-ion conductivity (in the range of 10^{-6} S/cm).
- Extensively studied, characterized and reproduced.
- Coating thickness can be varied by controlling the plasma deposition time.

Method of deposition

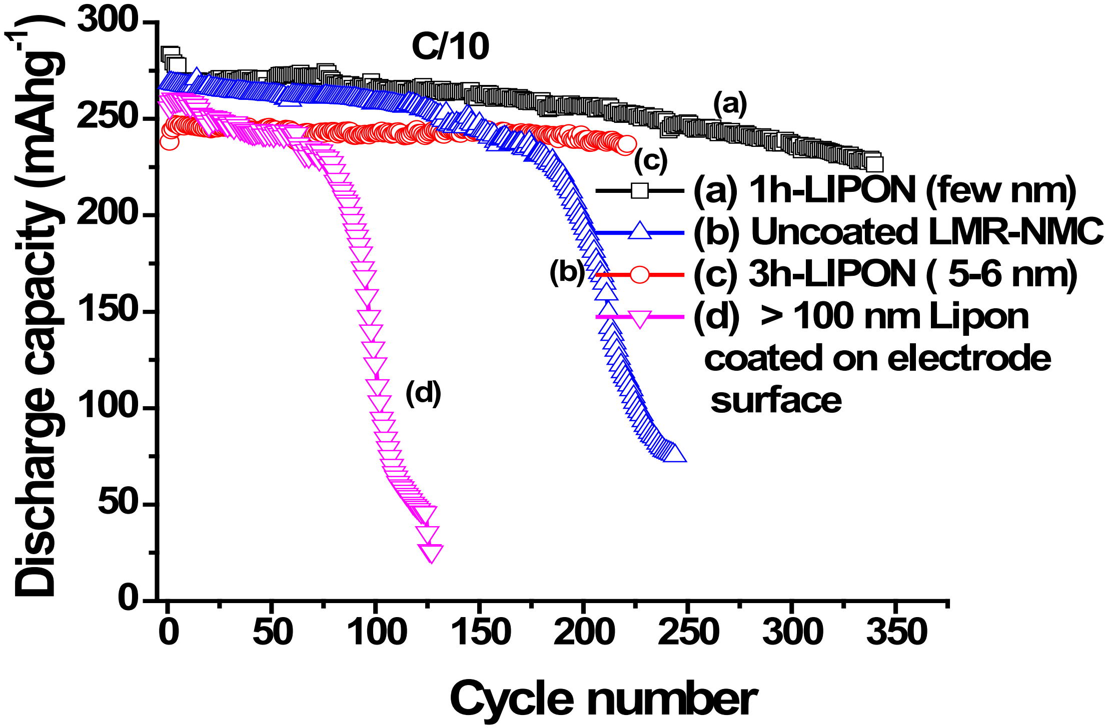
Lipon is deposited on LMR-NMC cathode materials as well as on electrodes using Rf-magnetron sputtering method

Typical Example : 1 hr deposition on cathode particles yields 1-2 nm
3 hr deposition > 5 nm

Also depends on the surface area, geometry and morphology of the particles

Technical Accomplishment:

(I) Effect of Lipon coating : Improvement in cycle life under high V cycling compared to pristine (uncoated)



Cycling window

4.9 – 2.5 V

Electrolyte : 1.2 M $LiPF_6$ in EC: DMC (1: 2 w/w)

Electrode composition: 85% LMR-NMC + 7.5% CB + 7.5% PVDF

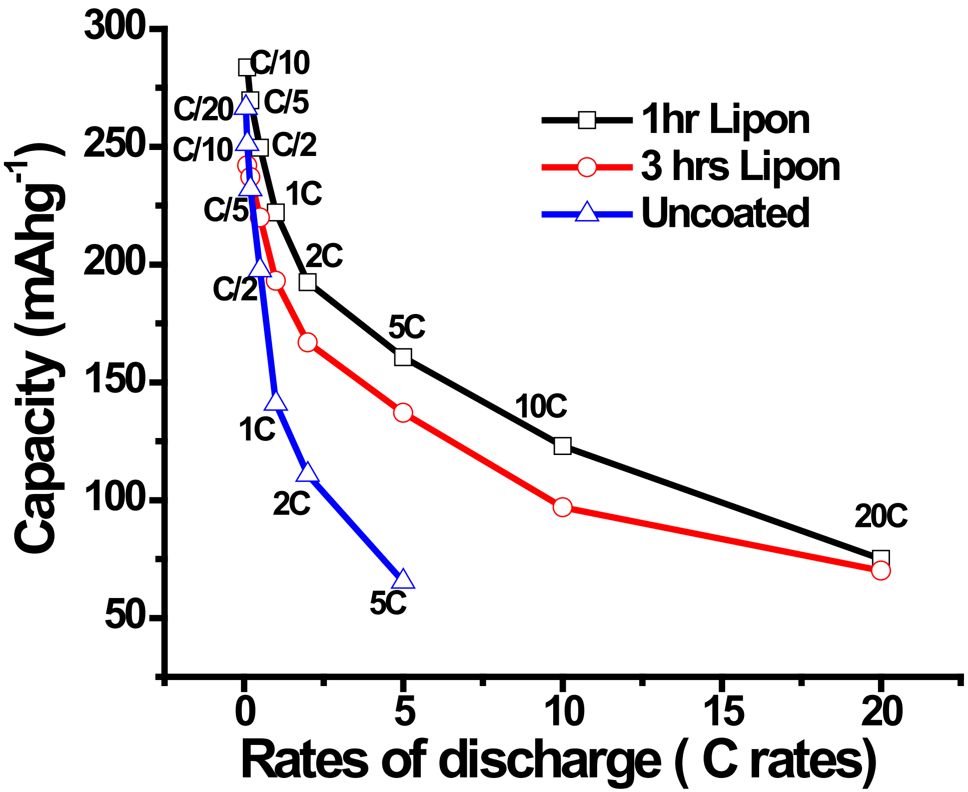
Experiments done in half-cell configuration(Li-metal) with similar loading and electrode composition.

Lipon is a good ionic conductor but is electronically insulating. Thick coatings affects capacity retention

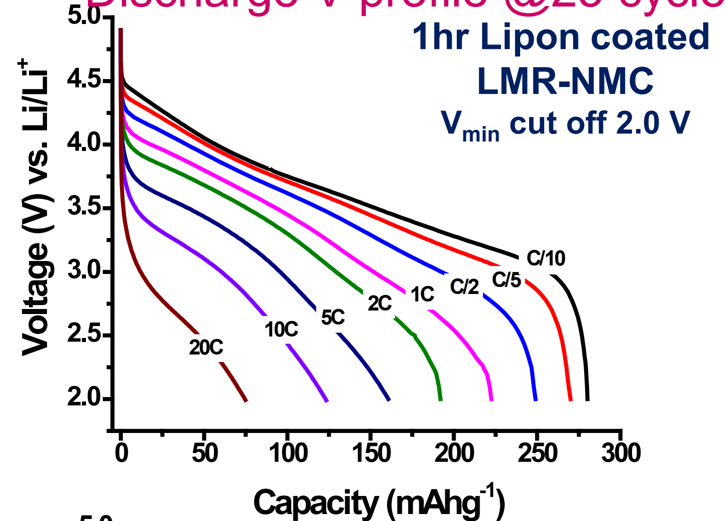
S. K. Martha et al. J. Mater. Chem. A 2013 (*in press*)

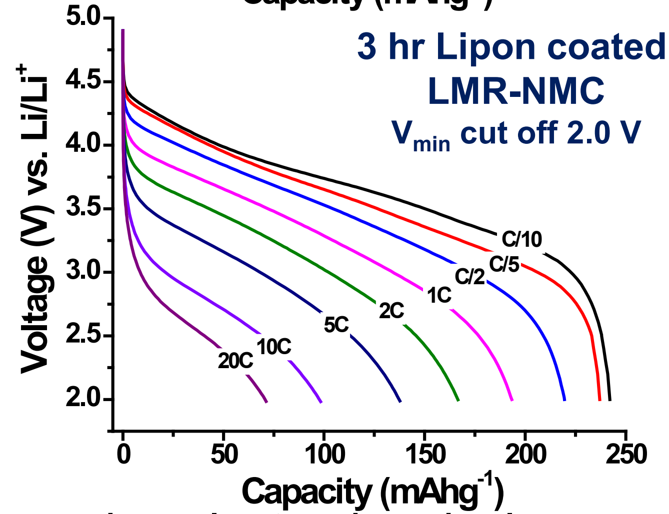
Technical Accomplishment

Effect of Lipon coating : Significant Improvement in C-rate performance under high V cycling compared to pristine (uncoated)



Discharge V profile @25 cycle





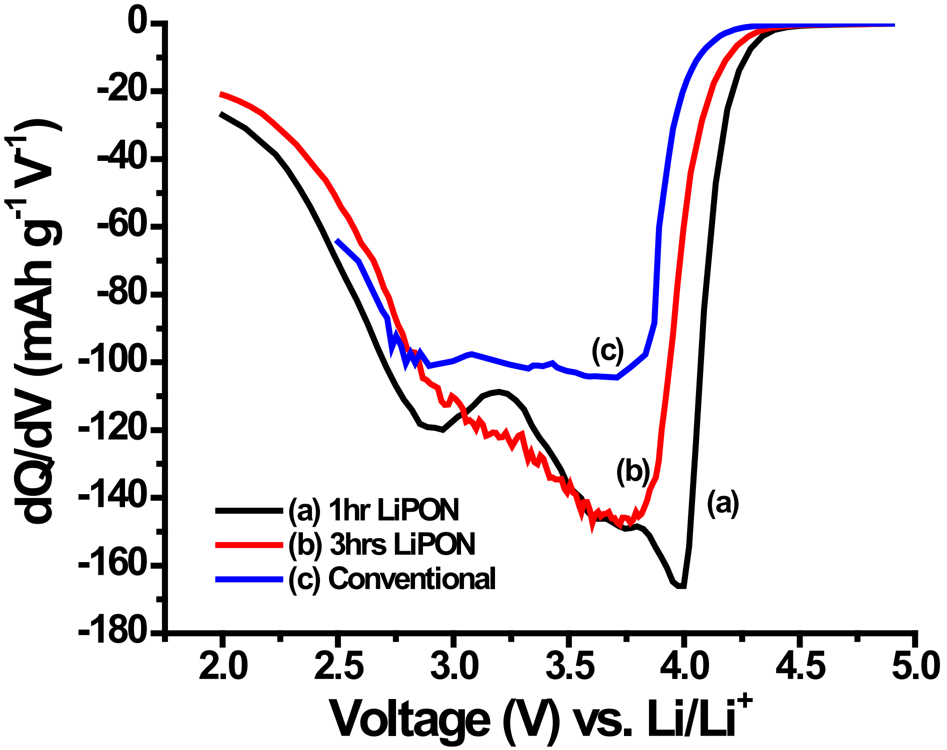
All capacity values normalized to V_{min} cut off 2.0 V

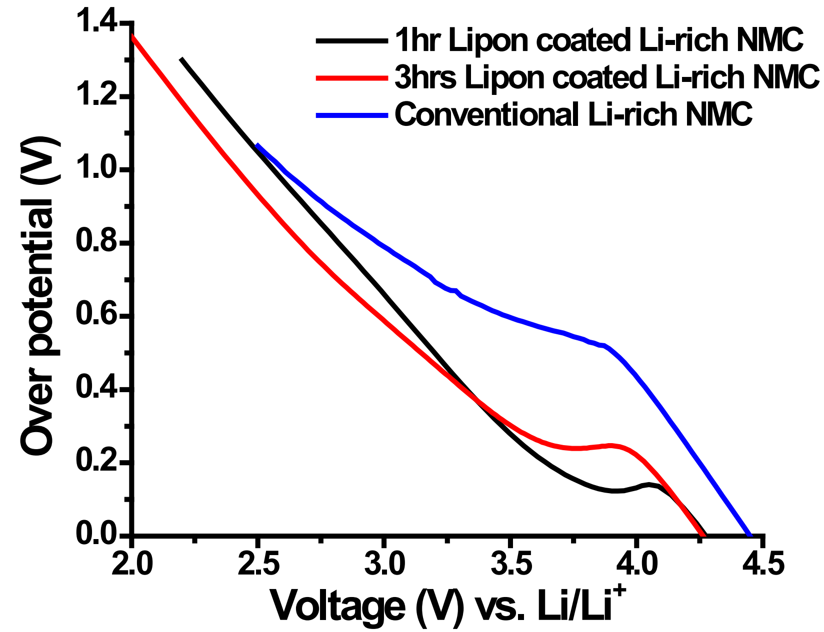
1 hours Lipon coating provides optimal thickness for improving electrochemical performance

S. K. Martha et al. J. Mater. Chem. A 2013 (*in press*)

Technical Accomplishment:

Lower electrode polarization observed for Lipon coated electrodes



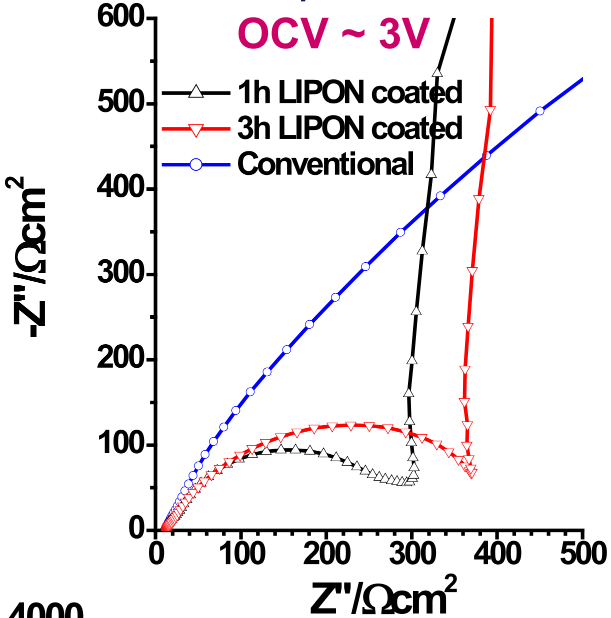


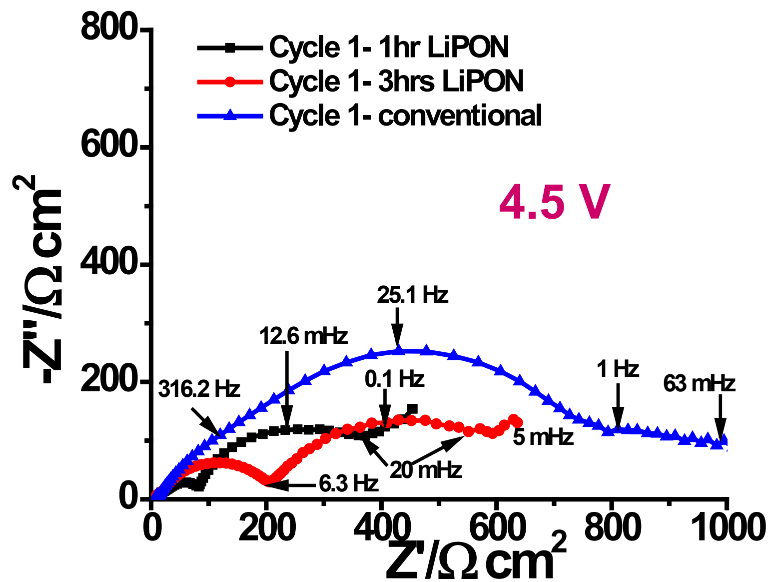
(e)

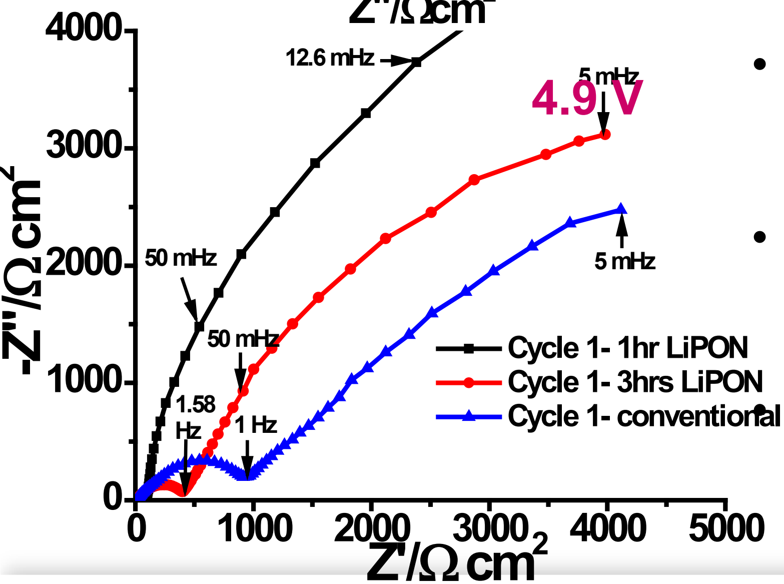
Significant shift in the dQ/dV plot to higher voltage for Lipon coated LMR-NMC.
Lipon coated cells showed lower overpotential due to lower charge transfer resistance.

Technical Accomplishment

EIS results show that presence of an optimal Lipon coating layer on LMR-NMC improves interfacial stability under high voltage cycling.







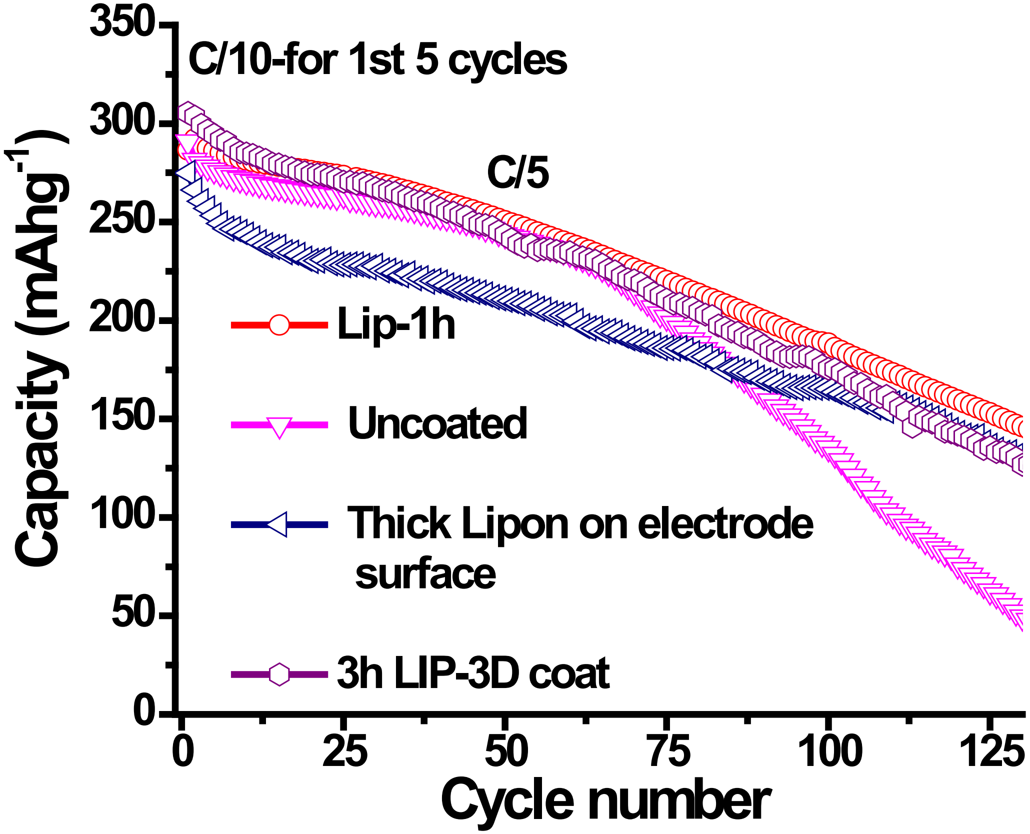
- Significant reduction in the charge-transfer (CT) resistance for Lipon coated electrodes.
- The trend continues for cells at intermediate & 100 % SOC.

I hr. Lipon deposition has the lowest CT resistance

S. K. Martha et al. J. Mater. Chem. A 2013 (*in press*)

Technical Accomplishment

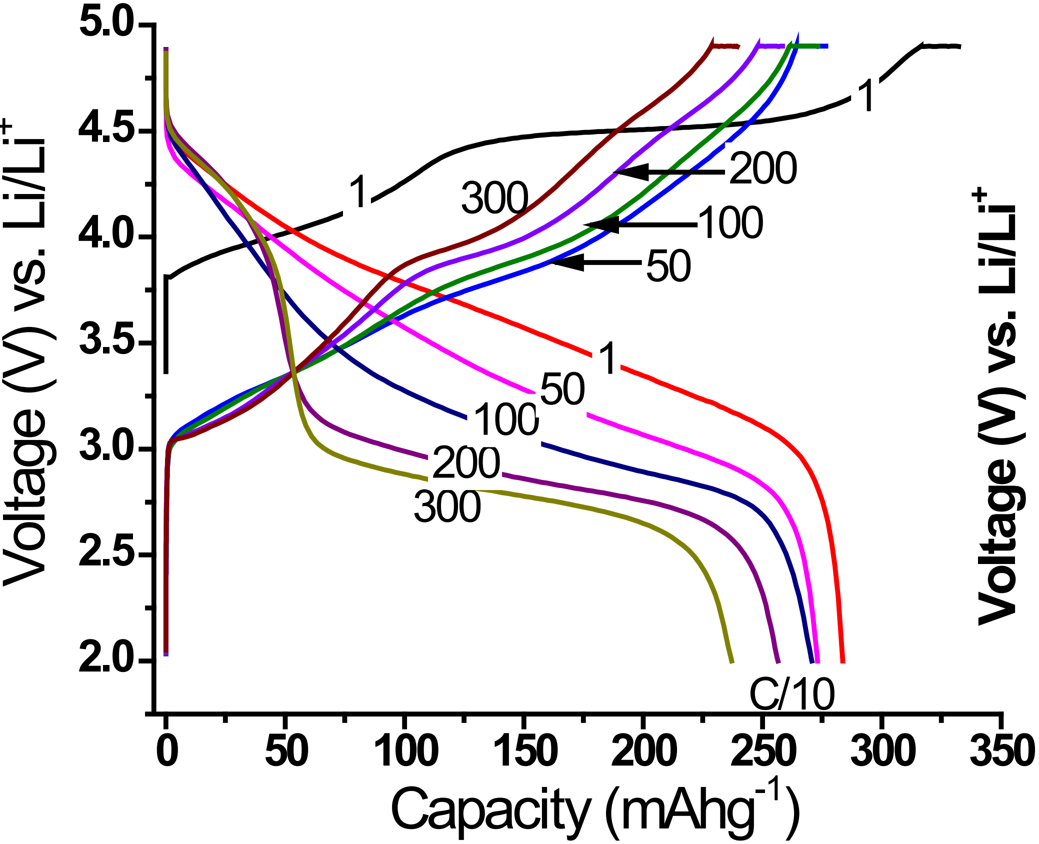
Lipon coating improves the capacity retention only at higher cycle numbers for cells cycled at 60 °C



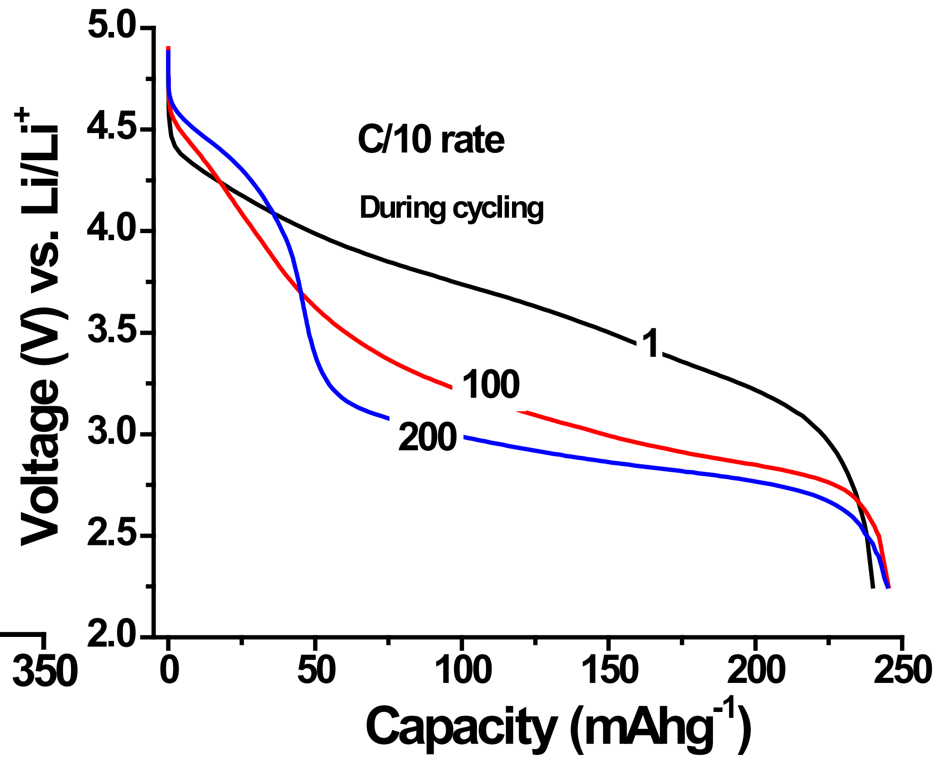
- Thicker and thinner coating have similar capacity retention on extended cycling at 60°C
- Hypothesis: Relatively lower Mn dissolution in coated electrodes at 60 °C; need to be checked independently by ICP measurements.

Technical Accomplishment

Voltage fade still observed for Lipon coated LMR-NMC when cycled up to 4.9V.



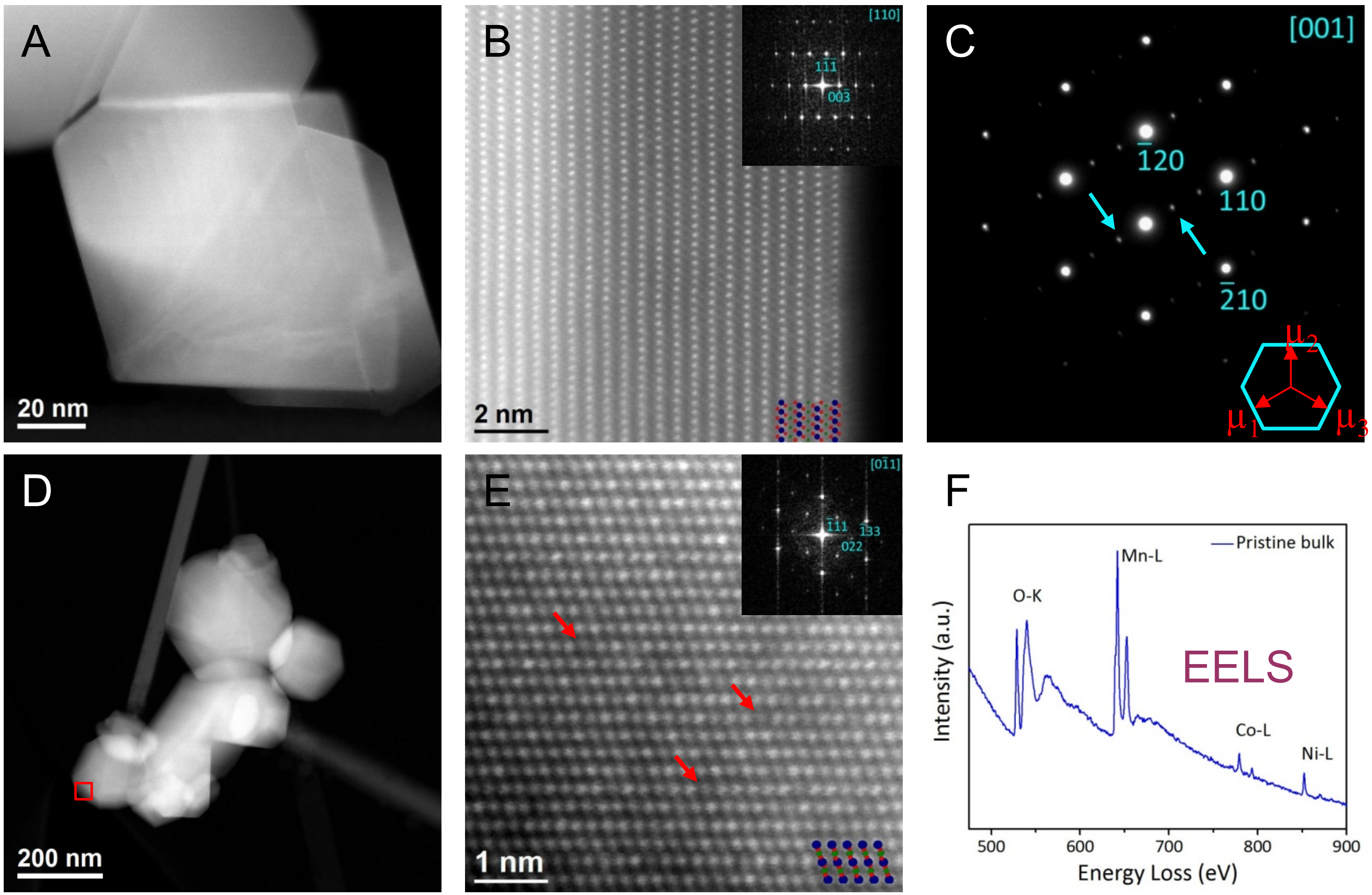
1-hr Lipon deposition



3-hr Lipon deposition

Technical Accomplishment

Uncycled or pristine LMR-NMC; $Li_{1.2}Mn_{0.525}Ni_{0.175}Co_{0.1}O_2$ showed majority hexagonal; R3m structure & minority monoclinic phase for the Li_2MnO_3 component

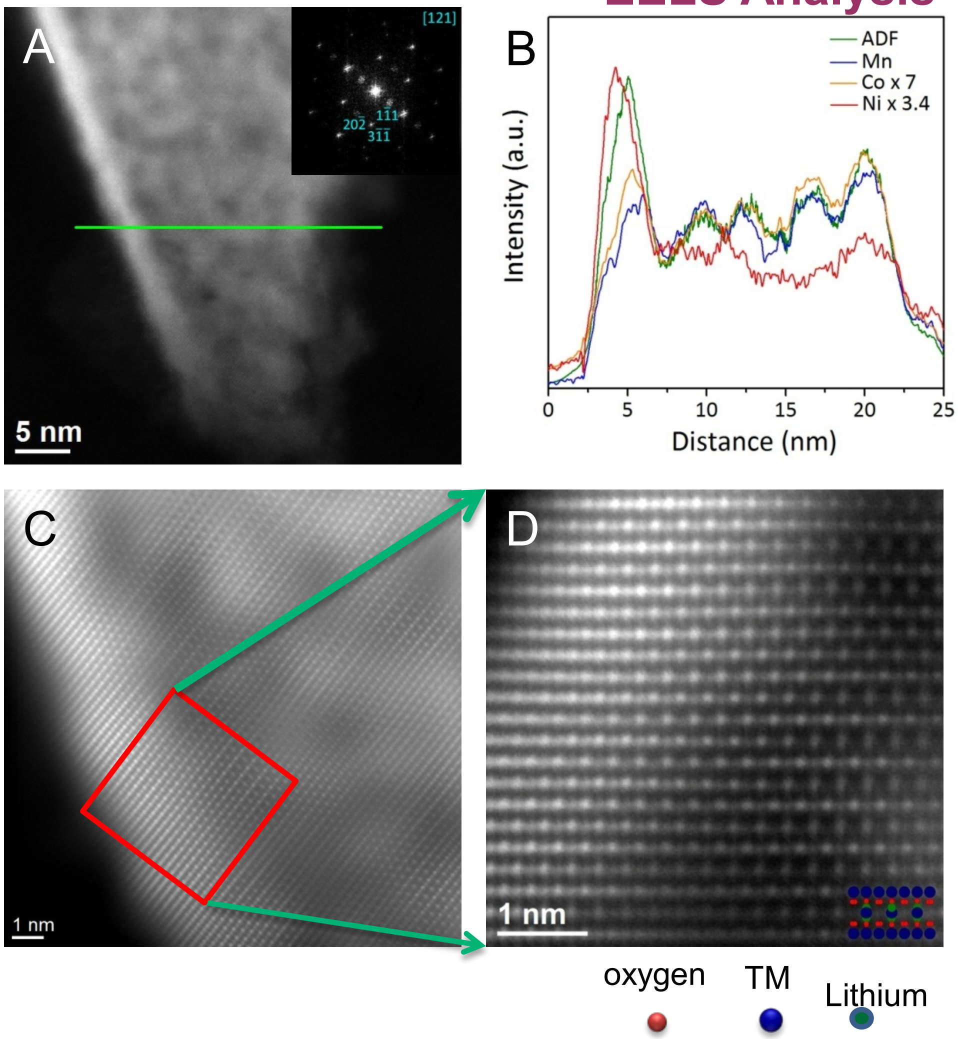


With Wu Zhou and Juan Carlos
ORNL (2012 unpublished)

Technical Accomplishment

LMR-NMC materials cycled 200 times between 4.9- 2V showed majority spinel like phase in the particle bulk

EELS Analysis



- FFT image can be indexed to the spinel phase along the [121] zone axis
- Suggests that structural changes could be a bulk driven process
- Increase TM metal at the surface . Ni is relatively higher. Mn and Co follow the same spatial pattern

Summary

- Electrochemical performance & EIS results show that presence of an optimal Lipon coating layer on LMR-NMC improves interfacial stability under high voltage cycling.
- Significant improvement in C-rate performance for Lipon coated LMR-NMC particles.
- Thicker surface coatings make particle surface insulating resulting in less capacity utilization.
- Coating improves cycle-life including at 60 ^{o}C cycling ; improves coulombic efficiency and 1st cycle irreversible capacity loss.
- We still notice voltage fade (or droop) in Lipon coated samples when cycled to 4.9 V (in half cells)

Collaborations and coordination with other institutions

- Quantifying voltage fade using ABR protocol and identify the role of coating. Argonne National Lab: *Daniel Abraham, Tony Burrell, Ali Abouramine & Ira Bloom.*

- Comparing Lipon coating method with more conformal coating approach such as atomic layer deposition (ALD) on LMR-NMC cathodes. NREL: *Robert Tenet & Chunmei Ban;* ORNL: *Nancy Dudney, G. M.Veith, Wyatt Tenhaeff*

- Electrode materials supplier : Toda America Inc.: Mr. Toyoji Sugisawa

- Cell level performance and failure analysis: Ford Motor Co., Research & Innovation Center: Andy Drews & Dawn Bernardi

- Synthesis/modification efforts in excess lithia NMC composition & similar high capacity couples. Argonne National Lab: *Chris Johnson & Vilas Pol*.

- Electrode characterization and spectroscopy. LBNL : *Robert Kostecki;* Stanford Synchrotron Research Laboratory, SLAC, CA : Dr. Joy Andrews & Yijin Liu

Future work

(i) Stabilizing the LMR-NMC phase without compromising on high capacity.

(i)Control of synthesis method, particle size, morphology and grain boundary interface (ii) Stabilizing the structure with dopants (isovalent substitution).

Effort also includes testing materials synthesized by industrial partners and national lab & universities.

(ii) Continue working on the capacity fade analysis at a full cell level for high voltage LMR-NMC cathodes(A-12 graphite & other anodes)

(iii) Continue local state-of-the charge (SOC) analysis on high energy lithium redox couples using micro-Raman, electron microscopy, x-ray & neutron studies (*ex situ* & *in situ*) to investigate capacity limiting mechanism.

Technical backup slides

Moving towards a common testing protocol for benchmarking results

ABR test protocol

Features	Details
Cell Configuration	Li metal as negative
Temperature	Room T
First Cycle	Recommended : 2-4.7 V; 10 mA/g
Cycling Method	2- 4.7 V; 20 mA/g Current interrupts (charge) at 3.5 V, 3.9 V (discharge) 4.7 V, 4.0V, 3.6V and 2.0V with 10 min rest to measure quasi OCV
Number of Cycles	> 20
Electrode Loading Electrolyte	6-7 mg/cm^2 1.2 M $LiPF_6$ in EC:DMC (1:2 w/w)

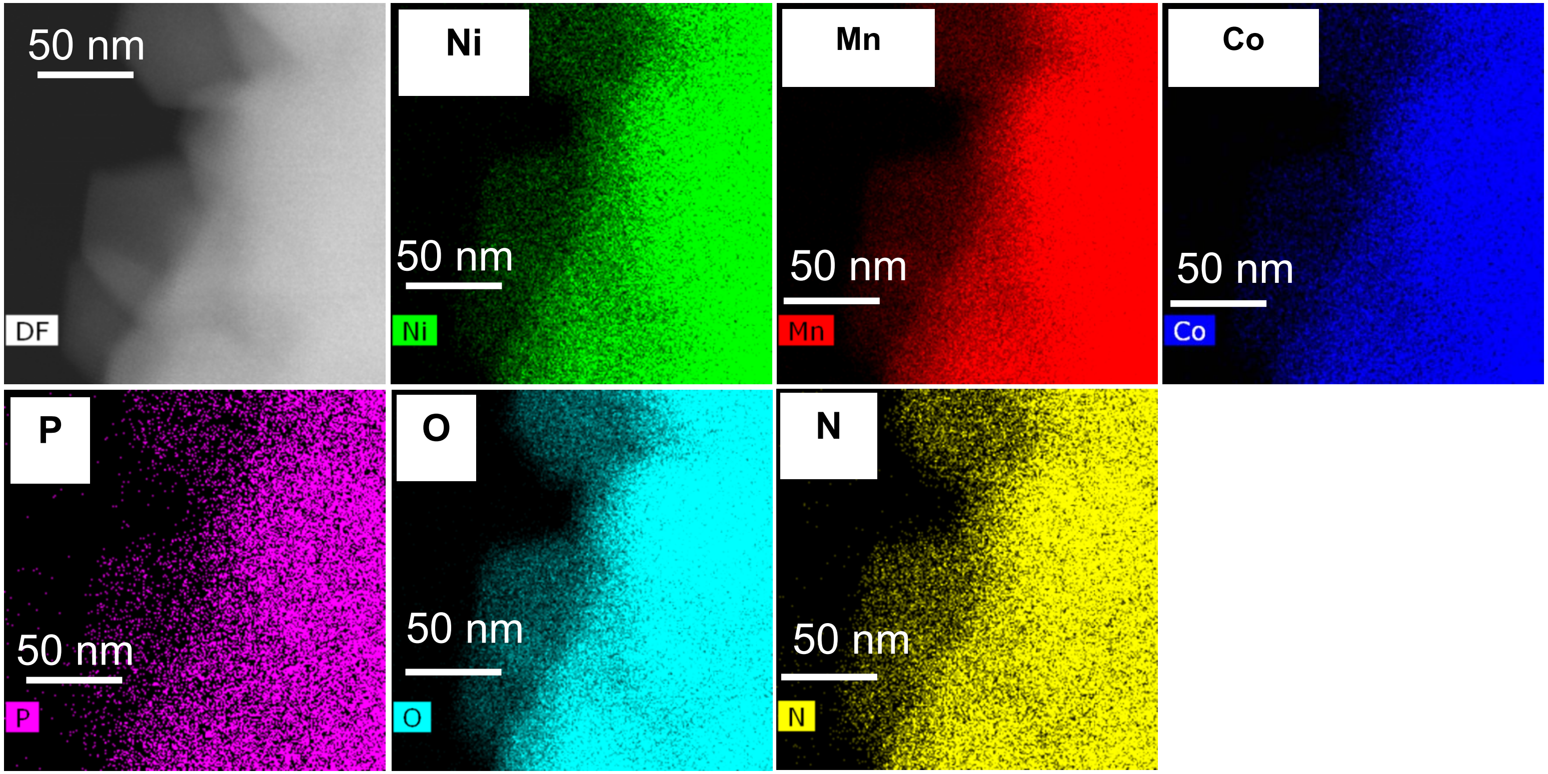
This Study

Features	Details
Cell Configuration	Li metal as negative
Temperature	Room T
First Cycle	2-4.9 V; 20 mA/g
Cycling Method	2- 4.9 V; 20 mA/g Both charge & discharge
Number of Cycles	> 20
Electrode Loading Electrolyte	6-7 mg/cm^2 1.2 M $LiPF_6$ in EC:DMC (1:2 w/w)

Courtesy : Tony Burrell & Daniel Abraham

Characterizing Lipon on the surface of LMR-NMC Particles

1: TEM with Elemental Mapping



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